



# **DEVELOPMENT OF A HYDROGEN-BASED ANNEALING PROCESS FOR THE DESULFURIZATION OF SINGLE CRYSTALLINE, NICKEL-BASED SUPERALLOY**

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**5 NOVEMBER 1994**

**FINAL REPORT**



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Prepared for  
Air Vehicle Department  
Materials Division (Code 434)  
NAVAL AIR WARFARE CENTER  
AIRCRAFT DIVISION WARMINSTER  
P.O. Box 5152  
Warminster, PA 18974-0591

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**19950605 000**

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# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

|   |  |   |                                   |   |  |
|---|--|---|-----------------------------------|---|--|
| 1. AGENCY USE ONLY (Leave blank)  |  | 2. REPORT DATE<br>5 NOVEMBER 1994                       |                                   | 3. REPORT TYPE AND DATES COVERED<br>FINAL                           |  |
| 4. TITLE AND SUBTITLE<br>DEVELOPMENT OF A HYDROGEN-BASED ANNEALING PROCESS FOR THE DESULFURIZATION OF SINGLE CRYSTALLINE, NICKEL-BASED SUPERALLOY   |  |   |                                   | 5. FUNDING NUMBERS  |  |
| 6. AUTHOR(S)<br>M. A. SMITH, T. H. MICKLE, W. E. FRAZIER, and J. WALDMAN  |  |   |                                   |   |  |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>Air Vehicle Department; Materials Division (Code 4342)<br>NAVAL AIR WARFARE CENTER; AIRCRAFT DIVISION WARMINSTER<br>P.O. Box 5152<br>Warminster, PA 18974-0591  |  |   |                                   | 8. PERFORMING ORGANIZATION REPORT NUMBER<br><br>NAWCADWAR-95001-4.3 |  |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)<br>Air Vehicle Department; Materials Division (Code 434)<br>NAVAL AIR WARFARE CENTER; AIRCRAFT DIVISION WARMINSTER<br>P.O. Box 5152<br>Warminster, PA 18974-0591  |  |   |                                   | 10. SPONSORING / MONITORING AGENCY REPORT NUMBER                    |  |
| 11. SUPPLEMENTARY NOTES   |  |   |                                   |   |  |
| 12a. DISTRIBUTION / AVAILABILITY STATEMENT<br><br>APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.   |  |   |                                   | 12b. DISTRIBUTION CODE  |  |
| 13. ABSTRACT (Maximum 200 words)<br><br>The presence of minor amounts of sulfur (1-10 ppm) in nickel-based superalloys has been associated with reduced oxidation resistance and premature spallation of protective coatings. A hydrogen annealing process has been developed by NAWCADWAR which effectively reduces the sulfur content of superalloys. The conditions which allow effective desulfurization are delineated. Diffusion of sulfur through the superalloy is found to be the rate controlling step for the process. |  |   |                                   |   |  |
| 14. SUBJECT TERMS<br><br>NICKEL-BASED SUPERALLOY, DESULFURIZATION, OXIDATION  |  |   |                                   | 15. NUMBER OF PAGES   |  |
|   |  |   |                                   | 16. PRICE CODE  |  |
| 17. SECURITY CLASSIFICATION OF REPORT<br>UNCLASSIFIED   | 18. SECURITY CLASSIFICATION OF THIS PAGE<br>UNCLASSIFIED | 19. SECURITY CLASSIFICATION OF ABSTRACT<br>UNCLASSIFIED | 20. LIMITATION OF ABSTRACT<br>SAR |   |  |

# NAWCADWAR-95001-4.3

## CONTENTS

|                               | PAGE |
|-------------------------------|------|
| FIGURES .....                 | i    |
| TABLES .....                  | ii   |
| INTRODUCTION .....            | 1    |
| EXPERIMENTAL PROCEDURE .....  | 2    |
| RESULTS .....                 | 3    |
| DISCUSSION .....              | 4    |
| Process Parameters .....      | 4    |
| Kinetics of the Process ..... | 4    |
| Cyclic Oxidation Tests .....  | 5    |
| CONCLUSIONS .....             | 6    |
| REFERENCES .....              | 6    |

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| DTIC TAB           | <input type="checkbox"/>            |
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## NAWCADWAR-95001-4.3

### FIGURES

|   | PAGE |
|---|------|
| Figure 1: Schematic of Hydrogen Annealing Fixture.....            | 8    |
| Figure 2: Schematic of cyclic oxidation furnace .....             | 9    |
| Figure 3a: Cyclic oxidation of "as-cast" Rene N6 @ 1200 C.....    | 12   |
| Figure 3b: Cyclic oxidation of desulfurized Rene N6 @ 1200 C..... | 13   |

### TABLES

|   |    |
|---|----|
| Table 1: Summary of parameters used in test matrix .....  | 7  |
| Table 2: Selected results from desulfurization anneals of a) Rene N6 b) Rene N5<br>c) PWA1484.....                            | 10 |
| Table 3: Estimated reduction of sulfur content as a function of temperature and composition<br>for a slab 75 mils thick ..... | 14 |

## NAWCADWAR-95001-4.3

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M.A. SMITH, T.H. MICKLE, W.E. FRAZIER, and J.WALDMAN

## INTRODUCTION

In order for a metal to withstand degradation by oxidation at elevated temperatures, a slow growing, compact, oxide film must form on the metal surface. Additionally, the film must not subsequently separate from the surface, thereby, exposing bare metal to the environment. Nickel-based superalloys commonly contain aluminum or chromium at concentrations sufficient to form scales of alumina, chromia, nickel chromium spinels and/or nickel aluminum spinels. In general, alloys which form aluminum containing oxides exhibit superior oxidation resistance in comparison to their chromium oxide forming counterparts[1,2]. This is due primarily to the lower diffusion of oxygen in the aluminum containing scales. Additional improvements in environmental resistance (as well as higher operating temperatures) have been achieved through the replacement of polycrystalline alloys with single crystal components, and the use of protective metal coatings such as NiCrAlY as well as with thermal barrier coatings (TBC) composed of ceramics such as yttria stabilized zirconia.

A common and serious short coming of these alloys is that loss of the protective oxide (or of the applied TBC) occurs on thermal cycling. As a result, the environmental resistance of the alloy is compromised resulting in accelerated oxidation of the alloy. In naval aviation environments, the service life of an alloy prone to spalling is more severely impaired by the phenomena of hot corrosion. At temperatures from 650-900°C, contact with Na<sub>2</sub>SO<sub>4</sub> leads to severe alloy degradation. (Na<sub>2</sub>SO<sub>4</sub> is formed by a reaction between NaCl, present as sea salt deposits and sulfur dioxide from engine exhaust). In laboratory tests, massive loss of superalloy cross section results after only a few hours exposure to molten Na<sub>2</sub>SO<sub>4</sub> at 900°C [3]. Non-spalling components are more resistant to the phenomena since they exhibit an incubation period in the presence of molten Na<sub>2</sub>SO<sub>4</sub> of several tens of hours prior to the onset of active corrosion [3]. An even longer incubation period (>400 hrs) may be achieved using alloys which form a compact chromia layer (i.e. Waspalloy) provided that the oxide does not spall [3]. Alumina layers are generally less resistant [3].

It is now well established that trace levels of sulfur (1-10 ppm) present as impurities in the bulk of nickel-based superalloys lead to the spallation phenomena described above [4-9]. It is believed that the sulfur impurity segregates as a monolayer at the metal/scale interface. This causes dramatically reduced adhesion and subsequent oxide spallation [10].

Traditionally, the problem has been controlled through the addition of elements such as yttrium and hafnium at levels of about 0.1 wt.%. These so-called "reactive" elements form

### NAWCADWAR-95001-4.3

refractory sulfides, thereby reducing the mobility of sulfur to very low levels. This effectively prevents the segregation of sulfur to the interface and eliminates oxide spallation. Most of the commercially available, nickel-based superalloys currently used for turbine engine blades contain such "reactive" additions.

There are several important problems with this approach. Generally, these additions are extremely expensive. Moreover, they make alloy processing more difficult and reduce casting yields[3,11]. In addition, there is some evidence that the sulfur-gettering effect is incomplete since oxide loss is sometimes observed (e.g. after ~500 hrs.) [12-14].

More recently, it has been shown that in some superalloys of very low bulk sulfur content ( $C_S \ll 1\text{ppm}$ ) the oxidation life is dramatically extended ( $t > 1200$  hrs. at  $1180^\circ\text{C}$ ) [3,13]. Further protection may be realized through the use of low sulfur NiCrAl coatings [3]. The service life of turbine blades fabricated from high purity alloys is limited by its fatigue or creep rupture life rather than by its environmental resistance. However, the commercial production of very low sulfur superalloys using ultrahigh purity elements is not generally feasible due to the high cost of these materials. Moreover, there is a pronounced tendency for the alloy to be contaminated with sulfur during the blade casting process.

This investigation centers on developing a commercially viable, hydrogen-based, annealing process for removing the sulfur from "as-cast" turbine blade components. Hydrogen reacts with sulfur at the superalloy surface removing it as hydrogen sulfide [11]. The process parameters studied included temperature, gas composition, furnace vacuum level, time, and gas flow rate. A test matrix of these variables was set up and used to optimize the "desulfurization" process. Some samples were chemically analyzed both before and after the treatments to determine their sulfur concentrations. Others were cyclically oxidized to determine whether the sulfur reductions were sufficient to produce adherent behavior.

### EXPERIMENTAL PROCEDURE

A process for removing sulfur from a commercially-supplied, nickel-based superalloy was designed by NAWCADWAR personnel (figure 1) [13]. Desulfurization is accomplished by annealing at high temperature in hydrogen. This allows removal of the sulfur as hydrogen sulfide gas. Due to the high reactivity of superalloys with oxygen and water, the hydrogen was flowed over a zirconium getter. Additionally, the annealing was done in a high vacuum, graphite furnace which allowed continuous evacuation of the flowing gases. Under proper operating conditions, the oxygen activity was low enough to prevent oxidation of the superalloy.

A molybdenum fixture was designed for use inside the furnace. This was intended to minimize hydrocarbon formation by reaction of hydrogen with the graphite heating elements and to prevent carburization of the superalloy slabs. The slabs were ground to specific thicknesses (see table 1), given a 1 mm diamond polish and degreased with

### NAWCADWAR-95001-4.3

acetone prior to annealing. The samples were suspended from sapphire hooks inside the chamber to prevent their reaction with the molybdenum components.

A Plackett-Burman experimental test matrix was used to establish the importance of the various processing parameters[15]. The variables tested included time, temperature, gas mixture, gas flow rate, vacuum level, and slab thickness. The values used are shown in table 1. This data was used to determine the optimum operating conditions for the process.

The alloys studied were Rene N5, Rene N6, and PWA 1484. All are proprietary, single crystal alloys produced by GE (Rene N5 & N6) or Pratt & Whitney (PWA 1484). None of the alloys studied contained yttrium gettering additions since this would impede sulfur removal. Initial and final sulfur levels were determined using Glow Discharge Mass Spectroscopy (GDMS). This technique is capable of accurately determining sulfur concentrations below the ppm level. (GDMS assessments were done by Charles Evans and Associates, Redwood City, CA and Shiva Technologies, Cicero, NY.) The sulfur concentration values were used to determine the apparent diffusion coefficient of sulfur in the alloys.

The environmental resistance of selected samples was evaluated using a cyclic oxidation furnace (figure 2). Oxidation samples were machined to dimensions of approximately 2cm X .25cm x .07 cm then given a 1  $\mu$ m diamond polish. Next, they were ultrasonically degreased using acetone and rinsed with dry methanol. Cycles consisted of holding the samples in air at 1200°C for 55 minutes followed by holding the sample for 5 minutes at room temperature. Samples were periodically removed and weighed. They were then returned to the furnace. Testing typically lasted for 200 cycles.

### RESULTS

The sulfur contents of each alloy, following desulfurization, along with the process parameters used are presented in tables 2a, 2b, & 2c. Evaluation of the data shows that effective desulfurization is favored by the use of higher vacuum, higher temperatures, thinner samples, and longer anneal times. Less important were the gas flow rates and the particular high purity gas mixture (10% H<sub>2</sub>-90% Ar versus 100% H<sub>2</sub>) employed. The use of standard purity gases leads to oxidation and prevents desulfurization.

Cyclic oxidation testing of Rene N6 at 1200°C confirms the correlation between low S content and improved oxidation resistance. For example, after 200 hrs, specimens with 4.3 ppm S experienced an average sample weight loss of 8.5 % vs 0.4% for a sample with .081 ppm S. Some desulfurized samples gave completely adherent scales in tests lasting up to 200-1hr cycles. (The small weight loss experienced by the .081 ppm S material was not the result of spalling to bare metal but was due to fracture within the oxide layer.)

In most samples, spalling ranging from 1-100% of the surface area was eventually observed. The measured weight losses of the alloys correlated fairly well with the residual

### NAWCADWAR-95001-4.3

sulfur content of the alloys. These data are summarized in figures 3a-b. The results generally indicate that a mostly adherent scale can be expected only when sulfur levels of about 0.25 ppm S are achieved. A transition to complete adherence occurs at around 0.1 ppm S.

## DISCUSSION

### Process Parameters:

An analysis of the desulfurization process variables shows that better desulfurization is achieved at a vacuum of 10 torr versus 125 torr. This is believed to be due to the tendency of the alloy to oxidize in the poorer vacuum. Any oxide thus formed is an effective barrier to desulfurization. The highest vacuum ( $10^{-4}$  torr) yielded no further improvement in desulfurization but is more expensive and difficult to maintain. The use of a Zr getter foil and the use of high purity gas mixtures (99.999% or better) were also essential in producing an oxide free surface. The 100%  $H_2$  gas had no discernible advantage over the 10%  $H_2$ -90% Ar. However, the latter mixture is perhaps more attractive owing to its lower cost and reduced explosion hazard. For cost reasons, the lower gas rate (10 scfh) is preferred over the higher flow rate (40 scfh). Thinner samples, higher annealing temperatures and longer annealing times all produced greater reductions in sulfur levels.

While the higher annealing temperature (1250°C) promotes improved desulfurization, it also increases the tendency of the second phase precipitates in the alloy (cuboidal  $\gamma$ - $Ni_3Al$ ) to coarsen. This may negatively impact the creep and fatigue resistance of the alloy. The use of higher temperatures also leads to an increased tendency for aluminum, nickel and chromium depletion from the surface. This results in an enrichment of refractory metals (Mo, Ta, and Re) at the surface. This layer must be removed to ensure a protective oxide is formed and to prevent damage to the mechanical properties of the alloy.

### Kinetics of the Process:

Consideration of the desulfurization data reveals that the process is controlled by the diffusion of sulfur through the alloy. Assuming an initially homogeneous distribution of sulfur in the alloy, the reduction in average sulfur concentration is readily calculated using the equation [16]:

$$C_{avg}/C_{initial} \sim (8/\pi^2) \cdot \exp(-\pi^2 D_s t/x^2)$$

where:  $C_{avg}$  = the average concentration of sulfur after desulfurization

$C_{initial}$  = the starting concentration of sulfur

$D_s$  = the diffusion coefficient of sulfur in the sample

### NAWCADWAR-95001-4.3

$t$  = annealing time

$x$  = the thickness of the sample

The diffusion of sulfur is considerably slower in these alloys than it is in pure nickel. The best estimates based on the desulfurization runs suggest that the values are from 1/3 to 1/2 those of nickel. An obvious consequence of this is that desulfurization of these alloys takes 2-3 times as long it would take in pure nickel.

The diffusion coefficient of nickel is given as [8]:

$$D_s = 1.4 \cdot \exp(-218,600/RT)$$

where:  $D_s$  = the diffusion coefficient of sulfur in nickel ( $\text{cm}^2/\text{sec}$ )

$$R = 8.314 \text{ joules/mol } ^\circ\text{K}$$

$$T = \text{temperature } ^\circ\text{K}$$

Superalloy turbine blades commonly have wall thicknesses of 1.8-2.0 mm (70-80 mils). The percent reduction of sulfur in a 1.9 mm (75 mils) thick slabs of a superalloy and of nickel as a function of time and temperature is shown in table 3. It is clear from these data that a much greater reduction of sulfur occurs in pure nickel than in the superalloy for a given annealing cycle.

#### Cyclic Oxidation Tests:

As discussed in the introduction, the oxidation resistance of these alloys is expected to be strongly dependent on the bulk sulfur levels. The results of this study were in accord with earlier work which showed that cyclic oxidation resistance is negatively impacted by the presence of trace impurities, notably sulfur. As discussed in the results section, a mostly adherent scale can be expected only when sulfur levels of about 0.25 ppm S are achieved. Given that the highest S levels recorded in the "as-cast" alloys were about 4.3 ppm S, this requires a factor of 16 reduction in the bulk sulfur levels. In a .075" thick slab containing 4.3 ppm S, it is estimated that an annealing time of 175 hours would be required (given  $D_s \sim 1.5 \cdot 10^{-8} \text{ cm}^2/\text{sec}$  @  $1250^\circ\text{C}$ .) In 50 hours (the longest time used in this study), the level would be reduced to approximately 1.7 ppm S (a factor of 2.5) and would not give reliable improvements in oxidation resistance.

## NAWCADWAR-95001-4.3

### CONCLUSIONS

- 1) Hydrogen desulfurization of nickel-based superalloys is strongly dependent on time, temperature, sample thickness, and gas purity. This last variable determines whether or not an oxide is formed on the surface.
- 2) Hydrogen desulfurization is a diffusion controlled process and is described by the equation for thick slab diffusion.
- 3) The diffusion coefficients of sulfur in the nickel-based superalloys studied are  $1/3$ - $1/2$  those of sulfur in pure nickel. As a result, annealing times 2-3 times those required for effective nickel desulfurization are required for the superalloys studied.
- 4) Sulfur levels of less than 0.25 ppm are required to produce reliable oxide adherence in Rene N6. Similar levels are probably needed in the other alloy systems studied. At current alloy purity levels, it would require from 150-300 hrs to achieve these levels in a 75 mil slab.

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| time (hrs) | temperature ( C) | gas mixture                 | vacuum (torr) | gas flow rate (scfm) | sample thickness (mm) | alloy    |
|------------|------------------|-----------------------------|---------------|----------------------|-----------------------|----------|
| 10         | 1200             | 100% H <sub>2</sub>         | 125           | 10                   | 0.51                  | Rene N6  |
| 30         | 1250             | 10% H <sub>2</sub> - 90% Ar | 10            | 40                   | 0.76                  | Rene N5  |
| 50         |                  |                             | 1X 10E-4      |                      | 1.6                   | PWA 1484 |
|            |                  |                             |               |                      | 1.9                   |          |

Table 1. Summary of parameters used in test matrix

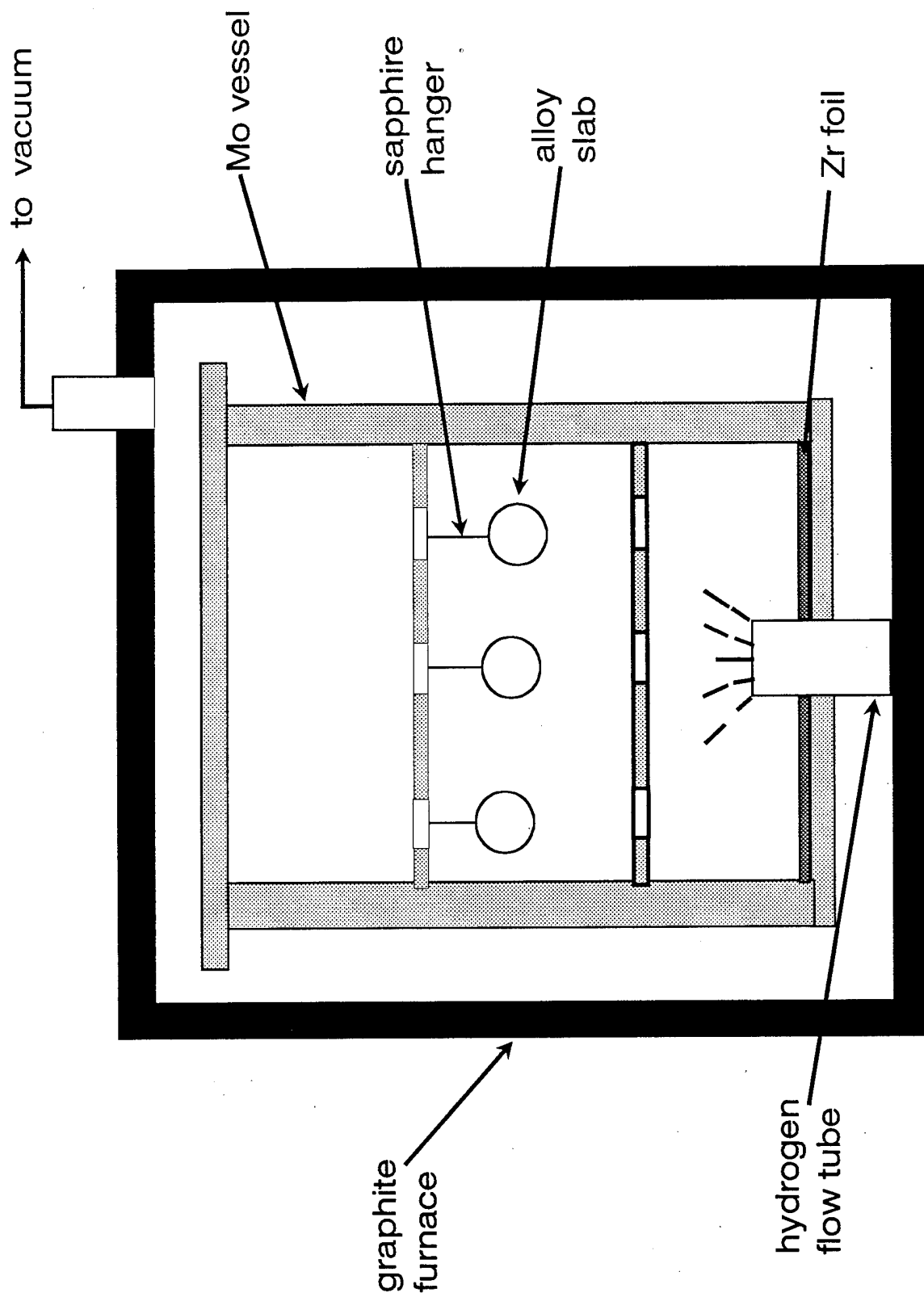


Figure 1: Schematic of Hydrogen Annealing Fixture

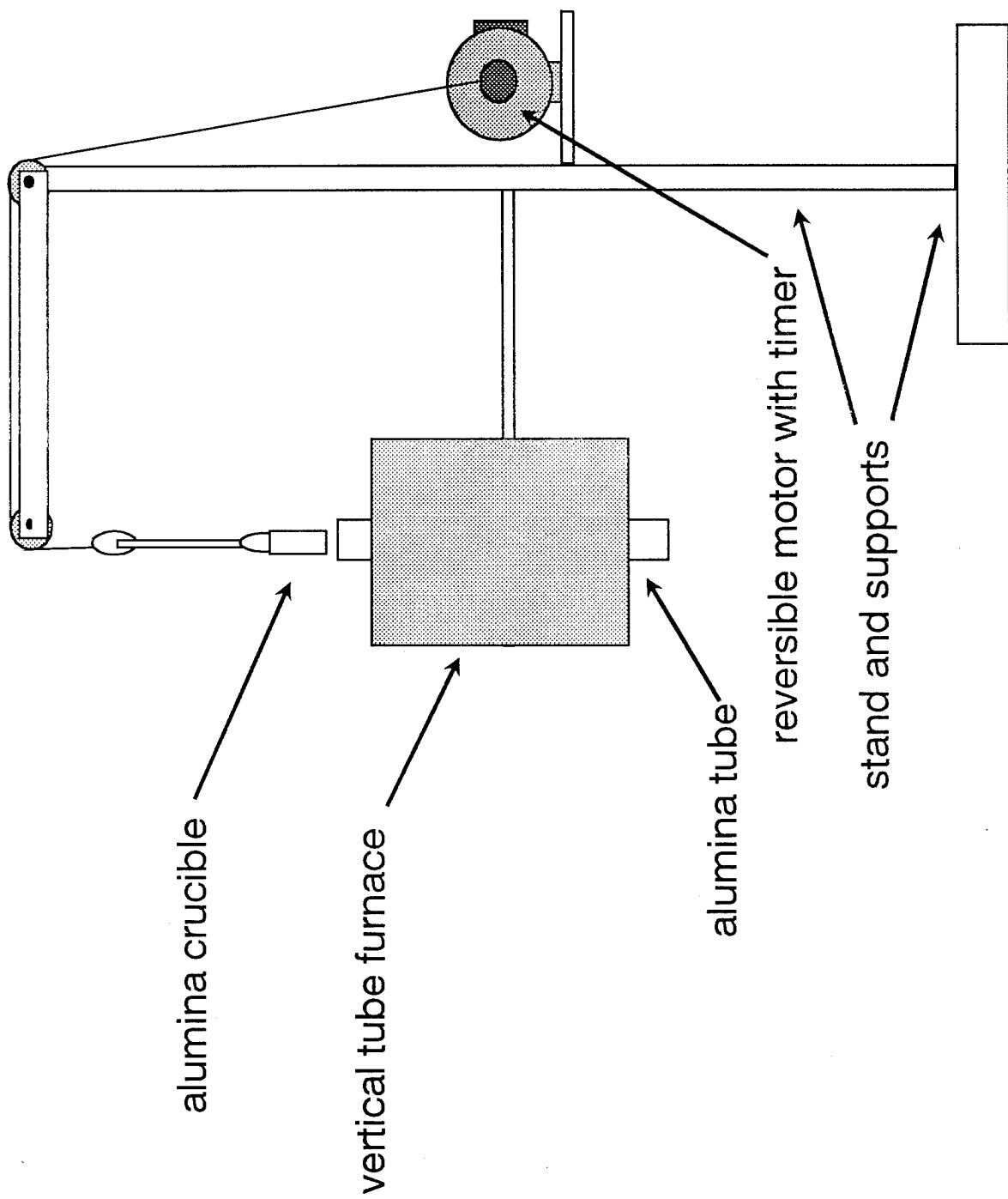


Figure 2: Schematic of cyclic oxidation furnace.

## NAWCADWAR-95001-4.3

a)

*RENE N6 SINGLE CRYSTAL*

| Heat # | Sample I.D. | Thick<br>(mils) | Temp (°C) | Time<br>(hrs.) | Atm<br>%H <sub>2</sub> | Gas flow<br>rate (SCFH) | Vacuum<br>(torr) | S (ppm)       |
|--------|-------------|-----------------|-----------|----------------|------------------------|-------------------------|------------------|---------------|
| 1A     | G1A         | 75              | -         | -              | -                      | -                       | -                | ?             |
| 1A     | G1A         | 75              | 1200      | 50             | 10%                    | 10                      | 10E-4 torr       | 1.2           |
|        |             |                 |           |                |                        |                         |                  |               |
| 325    | 325A        | 75              |           |                |                        |                         |                  | 2.7           |
| 325    | 325B        | 75              |           |                |                        |                         |                  | 1.1           |
| 325    | 325C        | 75              |           |                |                        |                         |                  | 2.1           |
| 325    |             | 75              |           |                |                        |                         |                  |               |
| 325    | 325-1       | 30              | 1250      | 30             | 10%                    | 10                      | 10 torr          | 0.081         |
| 325    | 325-2       | 30              | 1200      | 10             | 10%                    | 10                      | 10 torr          | 0.44          |
| 325    | 325-3       | 30              | 1250      | 10             | 100%                   | 40                      | 10 torr          | 0.26          |
| 325    | 325-4       | 30              | 1200      | 10             | 10%                    | 40                      | 10 torr          | 0.52          |
| 325    | 325-5       | 30              | 1250      | 30             | 100%                   | 10                      | 10 torr          | 0.12          |
| 325    | 325-6       | 30              | 1200      | 10             | 100%                   | 10                      | 125 torr         | 0.66          |
| 325    | 325-7       | 30              | 1200      | 30             | 100%                   | 10                      | 125 torr         | 0.43          |
| 325    | 325-8       | 30              | 1200      | 30             | 10%                    | 40                      | 125 torr         | 0.26          |
| 325    | 325-9       | 30              | 1250      | 30             | 10%                    | 40                      | 125 torr         | 0.24          |
| 325    | 325-10      | 30              | 1200      | 30             | 10%                    | 40                      | 10 torr          | 0.15          |
| 325    | 325-11      | 30              | 1250      | 10             | 10%                    | 10                      | 125 torr         | 0.96          |
| 325    | 325-12      | 30              | 1250      | 10             | 100%                   | 40                      | 125 torr         | 0.27          |
|        |             |                 |           |                |                        |                         |                  |               |
| 1      | B1          | 125             |           |                |                        |                         |                  | 1.6           |
| 1      | D1          | 20              | 1250      | 50             | 10%                    | 40                      | 10               | .036          |
|        |             |                 |           |                |                        |                         |                  |               |
| 3      | A3          | 125             |           |                |                        |                         |                  | 2.5           |
| 3      | D3          | 125             |           |                |                        |                         |                  | 2.5           |
|        |             |                 |           |                |                        |                         |                  |               |
| 4      | C4          | 125             |           |                |                        |                         |                  | 4.3           |
|        |             |                 |           |                |                        |                         |                  |               |
| 722    | D722        | 75              |           |                |                        |                         |                  | .091-<br>.095 |
| 722    | E722        | 20              | 1250      | 50             | 10%                    | 40                      | 10               | .016          |

b)

*RENE N5 SINGLE CRYSTAL*

| Heat # | Sample I.D. | Thick (mils) | Temp (°C) | Time (hrs.) | Atm %H <sub>2</sub> | Gas flow rate (SCFH) | Vacuum (torr) | S (ppm) |
|--------|-------------|--------------|-----------|-------------|---------------------|----------------------|---------------|---------|
| 1822   | K1822       | 75           | -         | -           | -                   | -                    | -             | 2.1     |
| 1822   | K1822       | 75           | 1250      | 50          | 10%                 | 40                   | 10            | 0.86    |
| 1822   | L1822       | 63           | 1200      | 50          | 10%                 | 10                   | 10E-4 torr    | 1.6     |
|        |             |              |           |             |                     |                      |               |         |
| 1055   | A1055       | 125          | -         |             |                     |                      |               | ?       |
| 1055   | A1055-1     | 30           | 1200      | 50          | 10%                 | 10                   | 10E-4 torr    | .19     |
| 1055   | A1055-2     | 60           | 1200      | 50          | 10%                 | 10                   | 10E-4 torr    | .63     |

c)

*PWA 1484 SINGLE CRYSTAL*

| Heat # | Sample I.D. | Thick (mils) | Temp (°C) | Time (hrs.) | Atm %H <sub>2</sub> | Gas flow rate (SCFH) | S (ppm) |                                       |
|--------|-------------|--------------|-----------|-------------|---------------------|----------------------|---------|---------------------------------------|
| 6594   | PWA         | -            | -         | -           | -                   | -                    | ?       |                                       |
| 6594   | PW1         | 15           | 1200      | 50          | 10%                 | 10                   | 0.51    |                                       |
| 6594   | PW2         | 30           | 1200      | 50          | 10%                 | 10                   | 1.1     |                                       |
| 6594   | PW3         | 80           | 1200      | 50          | 10%                 | 10                   | 1.9     |                                       |
|        |             |              |           |             |                     |                      |         |                                       |
| 7888A  | PWB         | 94           | -         | -           | -                   | -                    |         | tubular sample                        |
| 7888A  | PW8         | 94           | 1200      | 50          | 10%                 | 10                   | 9.5     | tubular sample                        |
| 7888A  | PW8A        | 65           | 1250      | 50          | 10%                 | 40                   | 1.8-2.6 | tubular sample<br>results<br>variable |

Table2: Selected results from desulfurization anneals of a) Rene N6 b) Rene N5  
c) PWA1484

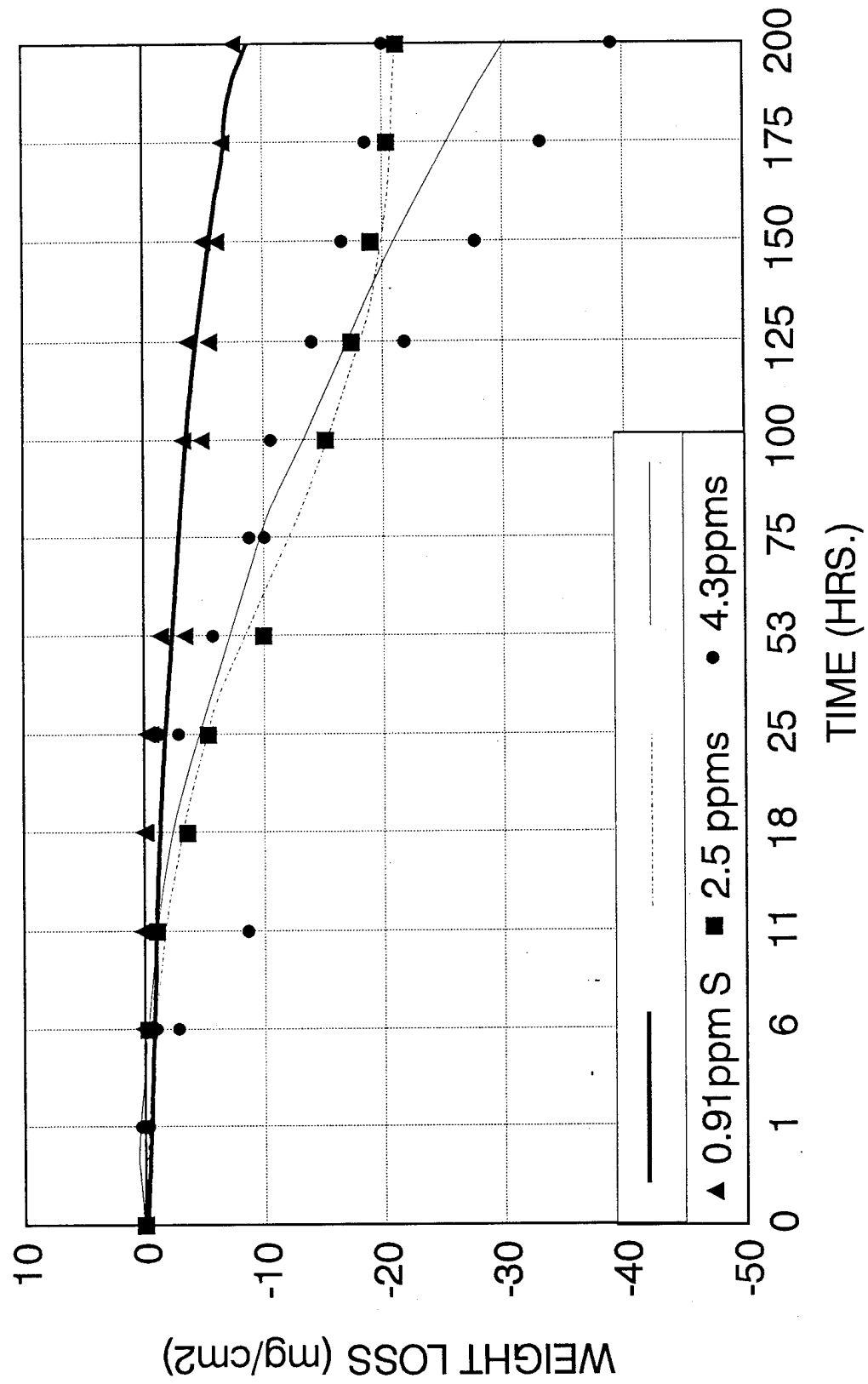


Figure 3a: Cyclic oxidation of "as-cast" Rene N6 @ 1200 C

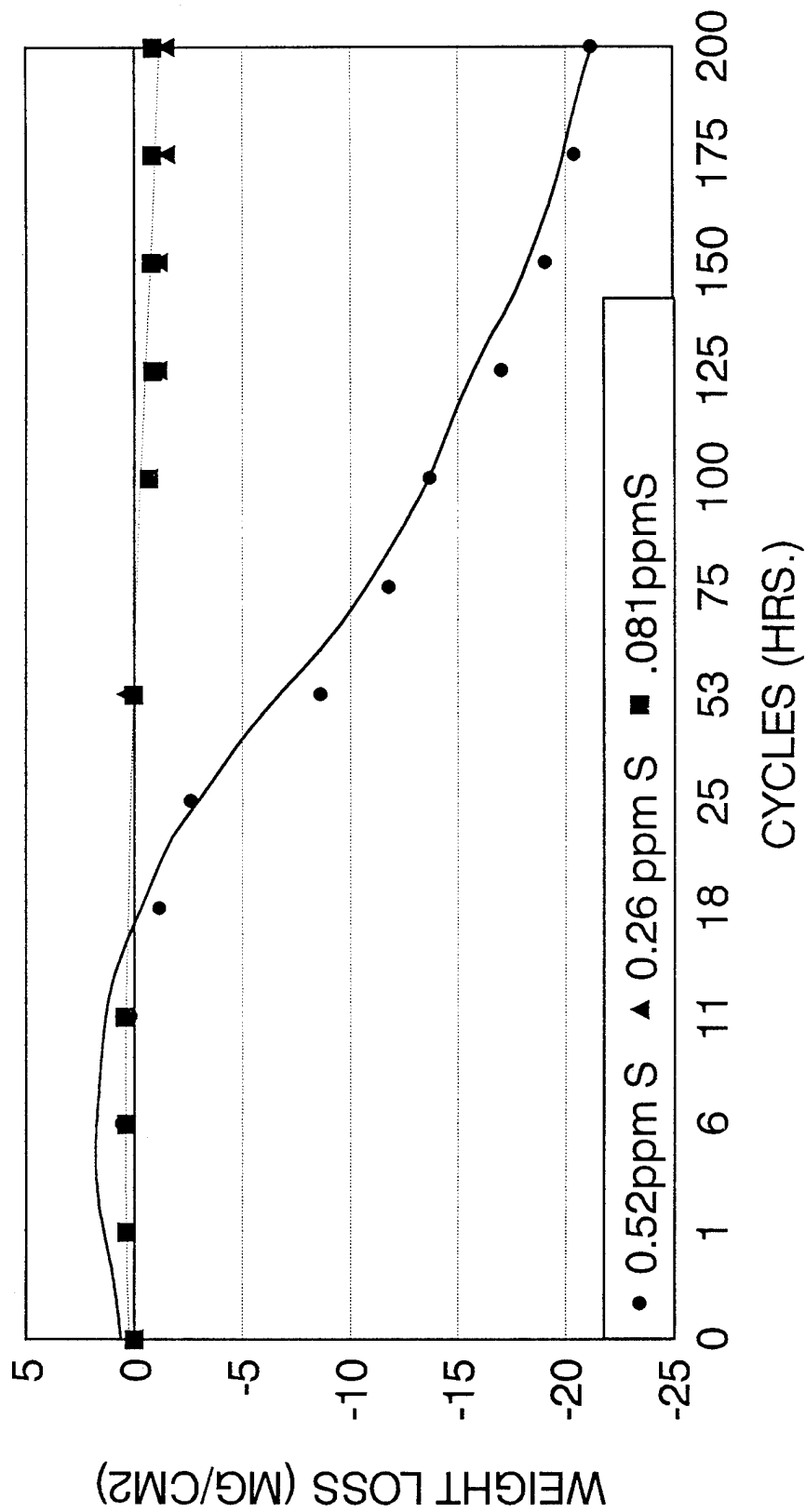


Figure 3b: Cyclic oxidation of desulfurized Rene N6 @ 1200 C

| Pure Nickel-Initial S concentration | after 50 hr. anneal @ 1200 C | ibid 1250 C |
|-------------------------------------|------------------------------|-------------|
| 10 ppm                              | 2.4 ppm                      | 0.92 ppm    |
| 5 ppm                               | 1.2 ppm                      | 0.46 ppm    |
| 2.5 ppm                             | 0.6 ppm                      | 0.23 ppm    |
| 1 ppm                               | 0.24 ppm                     | 0.12 ppm    |

| Initial Sulfur Concentration (Superalloy) | Concentration after 50hrs anneal @ 1200 C | ibid 1250 C |
|---|---|-------------|
| 10 ppm                                    | 5 ppm                                     | 4 ppm       |
| 5 ppm                                     | 2.5 ppm                                   | 2 ppm       |
| 2.5 ppm                                   | 1.25 ppm                                  | 1ppm        |
| 1 ppm                                     | 0.5 ppm                                   | 0.4 ppm     |

Table 3: Estimated reduction of sulfur content as a function of temperature and composition for a slab 75 mils thick..

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